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(ELECTROPOLISHING THE RARE-EARTH
METALS)

by

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ELECTROPOLISHING THE RARE-EARTH METALS

D. T. Peterson and E. N. Hopkins

ABSTRACT

This paper describes a method whereby the rare-earth metals can be consistently electropolished and chemically etched. The method involves cooling an alcohol-perchloric electrolyte to -76°C before electropolishing. The metals are chemically polished in the same solution.

INTRODUCTION

The rare-earth metals have gained increasing prominence in the last decade as basic research materials. In many metallurgical investigations, it is desirable to have methods of polishing the metal surfaces free of contamination. This is necessary for metallographic examination as well as x-ray examination. The two more successful methods for producing metal surfaces free from contamination are chemical and electrolytic polishing. The advantages of electropolishing vs other methods of surface preparation and specifically mechanical abrasion is principally in obtaining an unworked, strain free surface. The increasing use of the transmission electron microscope for the study of metals has also encouraged the study of electrolytic polishing.

Electrolytic polishing has been known¹ since 1925 with its metallographic aspects realized² in 1936 by Jacquet. Since 1936 there have been numerous investigations of polishing characteristics of electrolytes and their application to different metals.

The rare-earth metals are difficult to polish either chemically, mechanically, or electrolytically due to their tendency to oxidize, particularly in an aqueous solution. A method of electrolytic polishing would have to overcome this problem before any measure of success could be obtained. All of the rare earth metals with the exception of promethium and europium have been successfully electropolished by the method described in this work. A specimen of europium was not available to try. Yttrium was included because of its similarities to the rare earth metals.

EXPERIMENTAL PROCEDURE

The metals used in this investigation were samples received in the service laboratory and were not usually the purest metal obtainable. A direct current source capable of supplying up to 120 V and 3 A was used for electropolishing. The specimen surfaces to be electropolished were $1/4 \times 1/4$ in. The cathode was stainless steel. All electropolishing was done in a 250 ml open beaker on unmounted specimens. A magnetic stirrer was used to keep the solution at the desired temperature.

The electrolytes investigated were the following:
phosphoric acid, nitric acid, chromic acid, sulfuric acid, perchloric acid, sodium hydroxide, hydrochloric acid, oxalic acid and potassium hydroxide. Water, alcohol, ether and glycerine were used as solvents. The samples to be electropolished were ground through successively finer grit silicon carbide abrasive paper finishing with 600 grit paper.

After cleaning in absolute ethanol, the samples were electropolished at various times, temperatures and voltages. The current density could not be measured accurately because the current was always less than 0.02 mA and could not be read on the meter. The beaker containing the electrolyte was placed in a bath containing dry ice and acetone and the temperature of the solution was maintained at -76°C . The electrolyte was stirred at a moderate rate to insure a uniform and constant solution temperature.

DISCUSSION

The successful electropolishing solutions were the perchloric acid-alcohol types recommended by De Sy and Haemers.³ The nitric acid-alcohol mixtures showed some anodic brightening but were never as promising as the perchloric acid-alcohol mixtures. The most successful mixture was 1% perchloric acid in methanol. It should be observed that the perchloric acid-acetic anhydride solutions proposed by Jacquet would probably also be successful but are most expensive and more dangerous and therefore were not used in these experiments.

A solution of 1% perchloric acid in methanol was found to be successful on all of the metals. The time for complete polishing varied between 5 and 10 min at an open circuit voltage of 50 V with the longer polishing cycles not deteriorating the surface. The optimum temperature was found to be -76°C . At this temperature, the solution was not as chemically active as at room temperature thus allowing the metals to be electrolytically polished instead of chemically oxidized. Chemical

[oxidation appears to be an important factor in the electropolishing of metals. If the oxidation is very rapid, the electropolishing of the metal is retarded.] The rare earth metals are good examples of this behavior because of their rapid oxidation rate.

The mechanism of the rare-earth electropolishing is thought to be one of surface oxidation. A thick film is observed to be formed on some of the rare earths and can be collected on a copper grid and examined by electron microscopy selected area diffraction. A film formed on ytterbium was examined with the electron microscope and the diffraction pattern measured. This pattern corresponded to the structure of Yb_2O_3 as observed in x-ray diffraction analysis. The ytterbium sample was also observed during polishing using an optical microscope at 40 magnification. At the onset of polishing, a film is formed within a few seconds. The film adheres for a time and after one or more minutes begins to fall away from the surface of the metal. The metal appears to be bright and scratch free at this time. The stripping of the film is not consistent over the entire area of the metal surface. In some areas the film takes much longer to fall away than in other areas. This may be due to impurities such as oxide particles on the metal surface which tend to bind the film. Also the grinding scratches are somewhat nonuniform and some areas probably require longer polishing times to become flat and smooth.

[Chemical oxidation is the principle method of etching a metal surface for microscopic examination and the rare earths were etched in this manner. At room temperature, the nitric acid-alcohol mixtures]

(2 to 5% HNO_3) were found to be very rapid and difficult to control.

By cooling the nitric-alcohol solution to low temperatures, etching could be accomplished. However, it frequently left the surface of the metal uneven and spotty. The cause of the unevenness could have been the oxidation of the sample by air during the cleaning and drying operation after electropolishing. Therefore, the specimen was etched directly in the cold perchloric-alcohol electrolyte. Since perchloric acid is a strong oxidant, the etching characteristics should be essentially the same as with nitric acid. The perchloric-alcohol etching was accomplished simply by turning off the current and allowing the specimen to chemically oxidize for a sufficiently long time to reveal the structure. The time required for etching varied from 5 to 10 min. In order to re-etch a specimen that was insufficiently etched, it was necessary to electropolish for one minute prior to again chemically etching. All of the rare earth metals available were satisfactorily polished and etched by this procedure. The results of polishing the rare earths are seen in Figs. 1 through 14. All specimens were etched before photographing in the -76°C electrolyte.

CONCLUSIONS

The rare earth metals with the exception of promethium and europium have been successfully electropolished in a 1% perchloric acid - methanol mixture at very low temperatures. The mechanism by which polishing occurs appears to be a preferred oxidation reaction with peaks of the scratches oxidizing more readily than the troughs;

this oxidation eventually results in a smooth surface. The rare earth metals can be consistently chemically etched in the same electrolyte as used for electropolishing.

END

ACKNOWLEDGMENTS

The authors would like to acknowledge Messrs H. Baker and T. Roth and Miss Sandra Echols who helped with the experimental work.

REFERENCES

1. C. P. Madsen, United States Patent 1,562,710, November, 1925.
2. P. A. Jacquet, Nature 135, 1076 (1935).
3. De Sy and Haemers, Stahl und Eisen 61, 185-187 (1941).

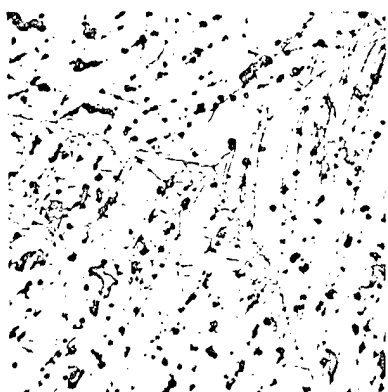


Fig. 1. Yttrium
x 250

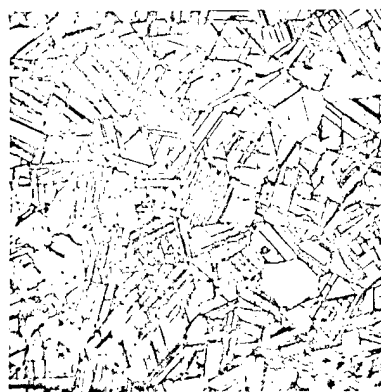


Fig. 2. Lanthanum
x 250

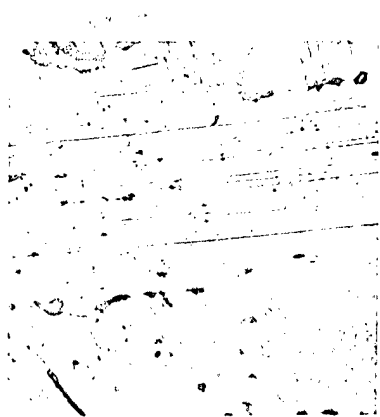


Fig. 3. Praseodymium
x 250

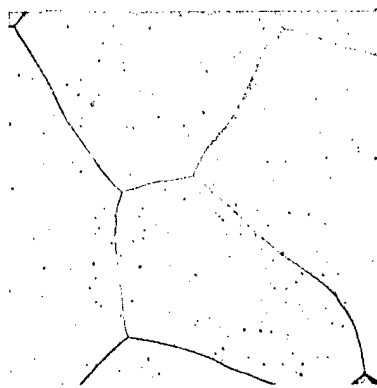


Fig. 4. Neodymium
x 250

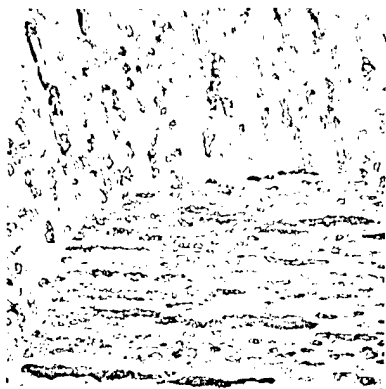


Fig. 5. Samarium
x 250

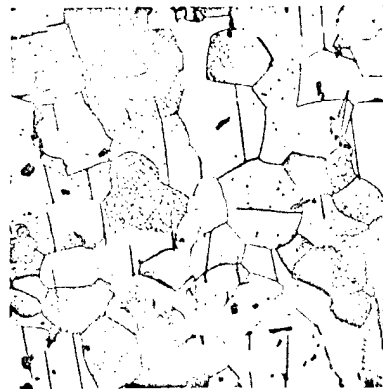


Fig. 6. Gadolinium
x 250

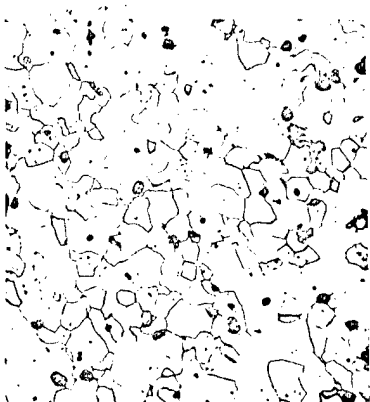


Fig. 7. Terbium
x 250

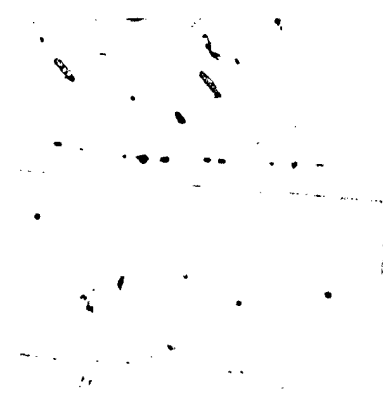


Fig. 8. Dysprosium
x 250



Fig. 9. Holmium
x 250



Fig. 10. Erbium
x 250

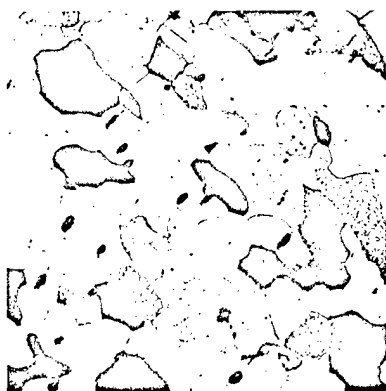


Fig. 11. Thulium
x 250

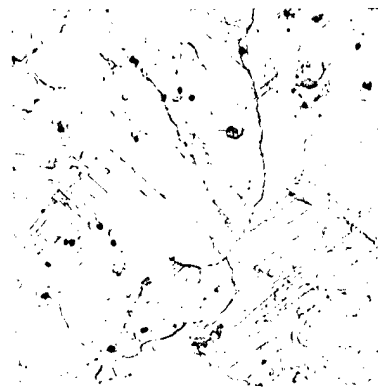


Fig. 12. Ytterbium
x 250

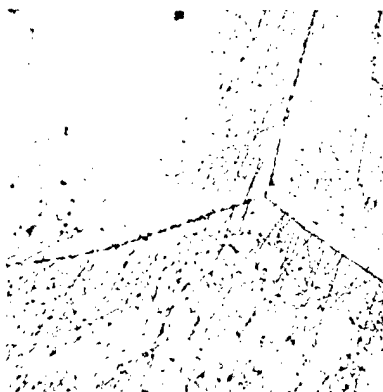


Fig. 13. Lutetium
x 250



Fig. 14. Cerium
x 250